

# Pyrolytic Formation Of Phenols From Some High Molecular Weight Tobacco Leaf Constituents And Related Non-Tobacco Materials<sup>1</sup>

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## Introduction

The simple phenols found in cigarette smoke are believed to be pyrolytic products of tobacco leaf constituents. Wenusch (16) suggested that these phenols arise from carbohydrate, lignin and polyphenolic material present in leaf. Ayres and Thornton (1) have shown that chlorogenic acid gives high yields of phenols on pyrolysis. Bell and co-workers (2) have recently suggested that carbohydrate materials which comprise about 55% of flue-cured leaf contribute about 41% of the phenol found in the mainstream of cigarette smoke.

The high molecular weight materials, cellulose, pectin, lignin and pigment comprise about 25% (8) of the dry weight of tobacco leaf, and may, therefore, individually or collectively, play an important role in phenol formation. Cellulose and pectin are essentially carbohydrates, the former a polyglucose and the latter a polygalacturonic acid; both lignin and pigment are known to contain benzene nuclei, the former in propylphenyl groups (3) and the latter in polyphenolic material (17). Considering structural characteristics and previous reports (2, 9, 12) in the

literature, one would expect the above-mentioned materials to yield phenols on pyrolysis, although not necessarily in similar amounts. In the present study, cellulose, pectin, lignin and pigment, isolated from tobacco leaf, were evaluated and compared with regard to their ability to produce phenols pyrolytically.

## Experimental

Cellulose (6), lignin (4, 11), pectin (13) and pigment (5) were isolated from Turkish tobacco by described methods, or slight modifications thereof. Cotton was obtained from Fischer Scientific Co.; wood lignin from Crown-Zellerbach Co.; citris pectin, polygalacturonic acid, glucose, glucuronic acid and cellobiose from Sigma Chemical Co.; isoeugenol from Eastman-Kodak Co.; and o-n-propyl phenol from Aldrich Chemical Co.<sup>3</sup>

Infrared spectra were obtained by the KBr pellet technique.

Lignin was oxidized in nitrobenzene and alkali (15), and the oxidation products were examined by paper chromatography (7).

Pyrolyses were conducted in a quartz tube (4' x 1.25" O.D.) packed with quartz chips. Temperature was maintained at 700°C with a Lindberg Hevi-Duty Furnace; nitrogen

generally served as the gaseous environment (30 ml/min). For certain experiments, pyrolytic temperatures were varied from 300-900°C in atmospheres of nitrogen and air.

Phenols were isolated from pyrolysates and their levels determined by previously reported procedures (10, 14). For pyrolysates from tobacco isolates, determinations were limited to phenol and m- and p-cresol (not resolvable by GLC) which were the major components in the phenolic fractions. For pyrolysates from non-tobacco materials, determinations included o-cresol. Total phenolic residues were determined from carefully dried aliquots of the phenolic fractions.

## Results and Discussion

Because known methods were used to isolate the high molecular weight tobacco leaf constituents, the assumption was made that the isolates were indeed lignin, pectin, and cellulose and would require only superficial characterization. In Figure 1 the infrared spectrum of tobacco leaf cellulose is compared to that of cotton cellulose. Figure 2 is a similar comparison of the infrared spectra of pectin from tobacco leaf and from citrus. Relatively high ash levels hindered the analysis of tobacco leaf lignin, but oxidation in alkali and nitrobenzene yielded the expected products: vanillin, syringaldehyde and p-hy-

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<sup>3</sup>Mention of a commercial item does not constitute endorsement by the United States Department of Agriculture over other items of a similar nature not mentioned.

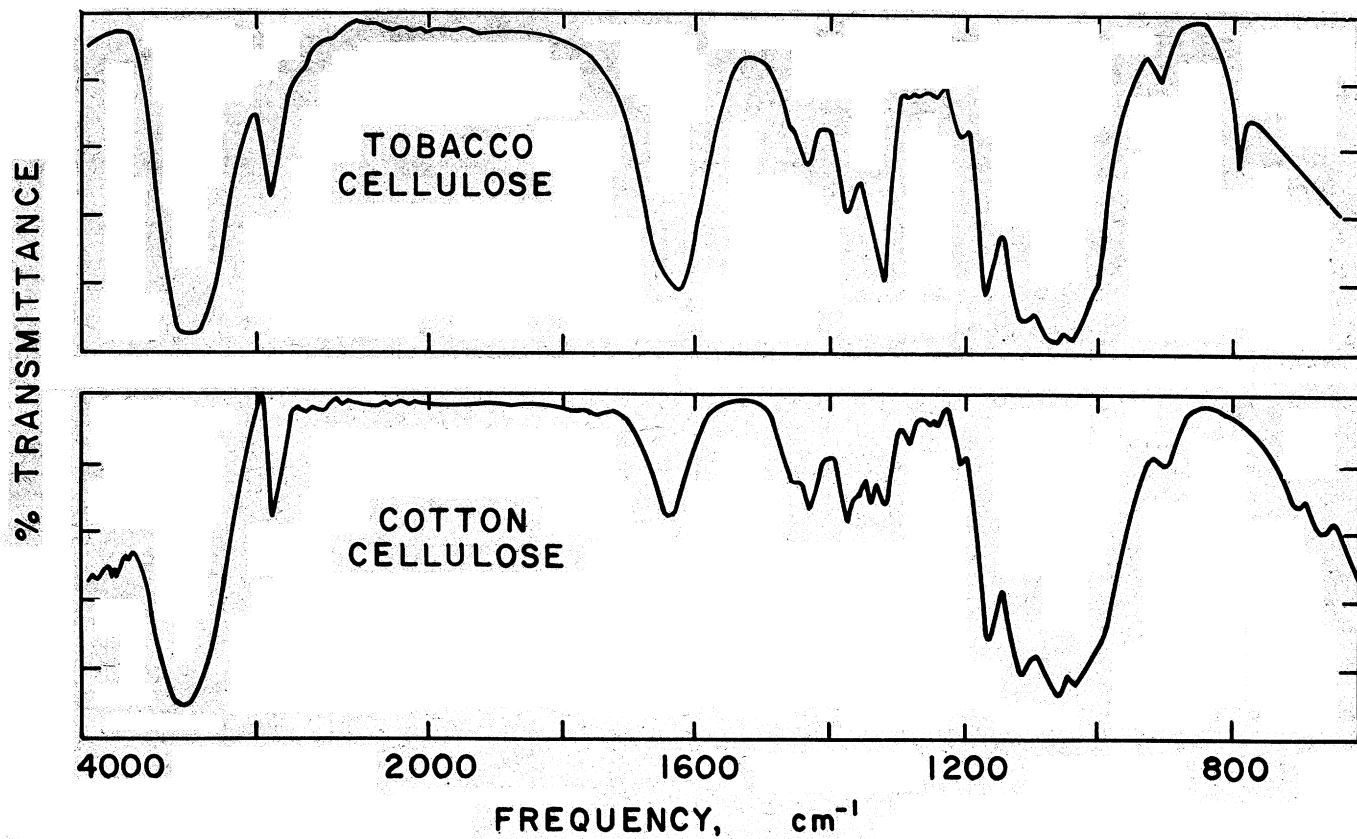


Figure 1. Infrared spectral comparison of cellulose isolated from tobacco and cotton.

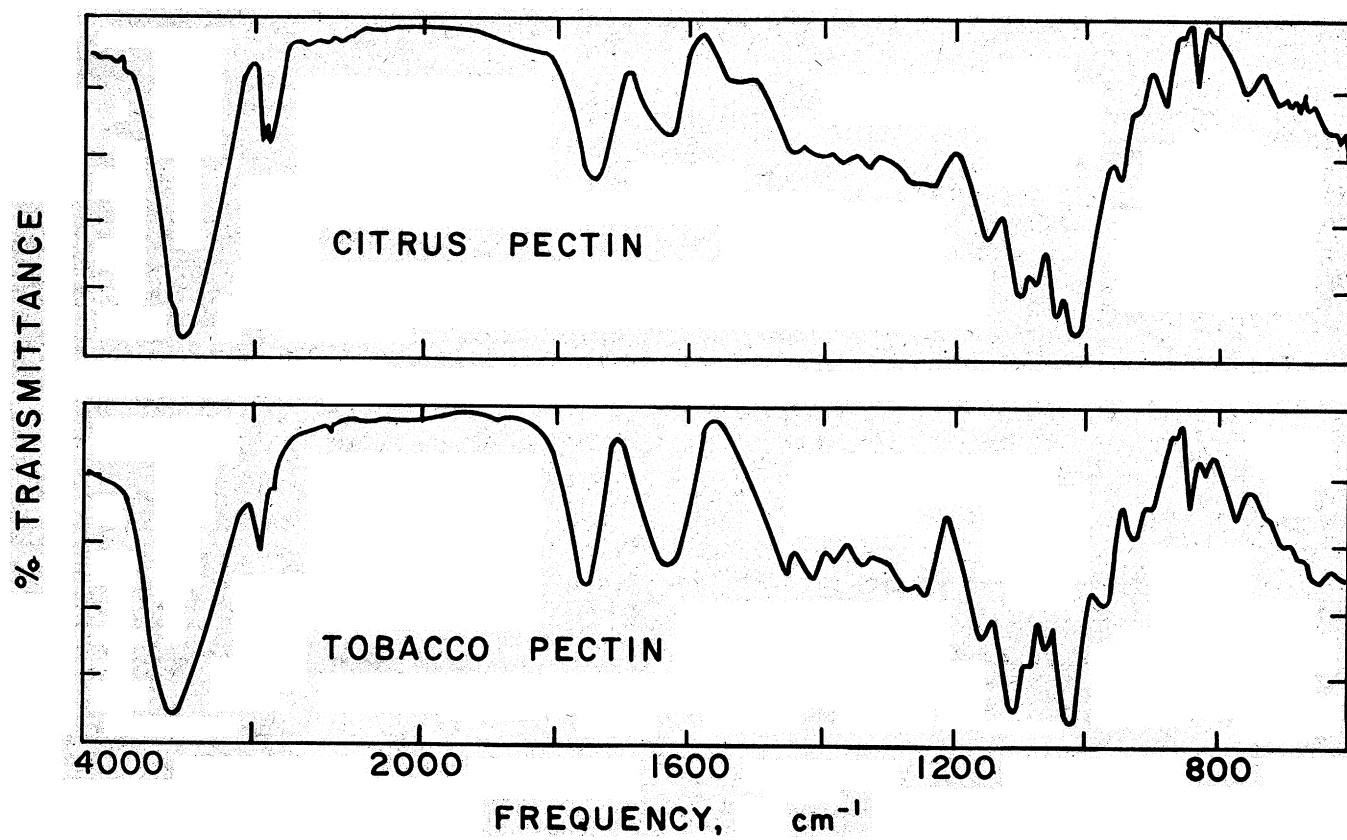


Figure 2. Infrared spectral comparison of pectin isolated from tobacco and citrus pectin.

droxybenzaldehyde (15). The pigment used in the present study has been characterized by Chortyk and coworkers (5).

Pyrolyses of the tobacco isolates yielded phenol and m- and p-cresol as the major phenolic products. Table 1 shows the levels of phenols obtained from the high molecular weight tobacco leaf constituents. The pyrolyses were conducted at 700°C under a stream of nitrogen. Turkish tobacco was pyrolyzed under the same conditions for comparative purposes. The high levels of phenols obtained from the Turkish tobacco pyrolysate as compared to that obtained from cigarette smoke condensates (14) can be attributed in part to the absence of combustion processes under the anaerobic experimental conditions used. Tobacco pigment was the most efficient phenol precursor<sup>4</sup> of the materials tested. Cellulose was a poor phenol precursor, while lignin and pectin (from tobacco) were relatively good phenol-formers.

Cellulose, lignin, pectin and polygalacturonic acid obtained from commercial sources were pyrolyzed under the same conditions (700°C, N<sub>2</sub>). The trend observed was similar to that of the analogous tobacco isolates. Lignin was the most effective, and cellulose the poorest phenol precursor (Table 2). The high yield of cresols from wood lignin is compatible with proposed structural characteristics of lignin. Pyrolysis of o-n-propyl phenol (Table 3), which may be similar to the type of recurring propylphenyl unit in lignin, yielded o-cresol as the major product, fission occurring primarily between C<sub>1</sub> and C<sub>2</sub> of the side chain. Isoeugenol, which like o-n-propyl phenol, may be regarded as a model lignin compound, similarly gave rise to high levels of cresols upon pyrolysis.

Certain other low molecular weight materials related to polymeric carbohydrates were also pyrolyzed under identical conditions (Table 3). The data indicate that carbohydrates, whether in the form of mono-, di- or polysaccharides, are relatively poor phenol precursors, although the behavior of tobacco leaf pectin unlike pectin from other sources is anomalous and difficult to interpret.

To determine the optimum conditions of phenol formation from wood lignin, for example, the latter material was pyrolyzed at temperatures ranging from 300-900°C, both in

**Table 1. Phenols from high molecular weight tobacco isolates**

Isolate pyrolyzed (700°C, N <sub>2</sub> )	Phenols (mg/100 g)	
	Phenol	m- and p-Cresol*
Pigment	94	80
Lignin	63	41
Pectin	67	30
Cellulose	6	2
Turkish tobacco**	105	25

\*Meta and para cresol were not resolvable by GLC.

\*\*Data for Turkish tobacco are shown for comparative purposes.

**Table 2. Phenols from non-tobacco high molecular weight substances**

Substance pyrolyzed (700°C, N <sub>2</sub> )	Phenols (mg/100 g)		
	Phenol	o-Cresol	m- and p-Cresol
Wood lignin	61	30	117
Polygalacturonic acid	14	7	8
Citrus pectin	12	6	8
Cotton (cellulose)	6	2	2

**Table 3. Phenols from certain low molecular weight materials**

Compound pyrolyzed (700°C, N <sub>2</sub> )	Phenols (mg/100 g)		
	Phenol	o-Cresol	m- and p-Cresol
o-n-Propylphenol	1,600	13,400	—
Isoeugenol	305	415	1,440
Cellobiose	31	9	11
Glucose	27	7	5
Glucuronic acid	18	4	5

nitrogen and in air. Total phenolic residue was determined after each pyrolysis. Figure 3 illustrates the pattern obtained. Maximum formation of phenols occurred in the 500°-600°C region. In an atmosphere of air, the pattern was similar to that obtained in nitrogen, but yields were lower. Measurement of yields of individual phenols (guaiacol, phenol, m- and p-cresol) at various temperatures indicated that 500°C was generally the temperature of maximum formation for these compounds, as well.

Although the present report evaluates the phenol-forming potential of certain high molecular weight materials, it is necessary to consider the relative proportions of these materials in leaf before reaching any conclusions regarding their contribution to the phenol content of cigarette smoke. Whereas pigment is by

far the most efficient precursor, it amounts to only 4% of the dry weight of leaf (5). Carbohydrates, including cellulose, comprise about 50% of the leaf (8), but are generally poor phenol precursors. Lignin, another good precursor, amounts to 3.5% of the leaf (8).

Preliminary experiments in this laboratory indicate that many types of compounds may serve as phenol precursors, such as certain non-volatile organic acids and proteinaceous material. We can only conclude, at this time, that many processes may be involved in phenol formation, and that structural requirements for phenol formation may be minimal, and may depend, to some extent, on temperature and gaseous environment.

## Summary

The effectiveness of certain high

<sup>4</sup>In the present study, the term phenol precursor denotes any material that on pyrolysis is converted to phenol; the degree of conversion is a measure of the relative efficiency of a given precursor.

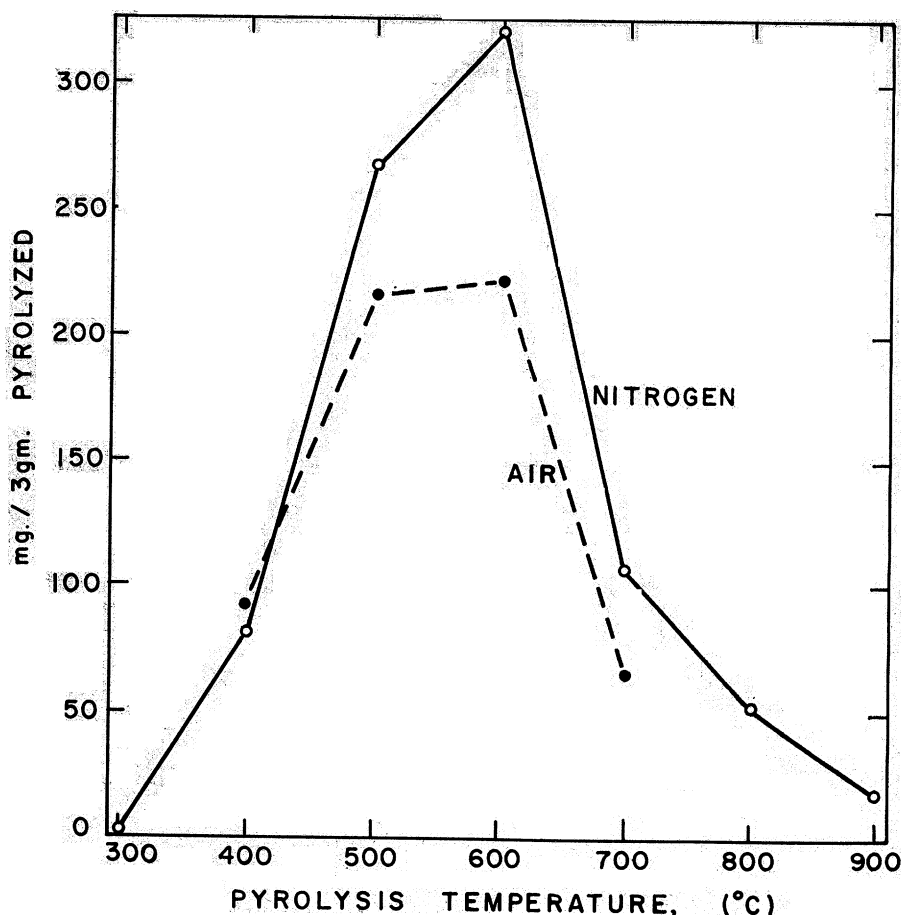


Figure 3. Effect of temperature on pyrolytic yield of total phenols from wood lignin.

molecular weight materials, isolated from tobacco leaf, to produce phenols pyrolytically was evaluated. Pigment was shown to be the best phenol precursor and cellulose the poorest. Commercially available lignin, pectin and cellulose followed a trend similar to their tobacco analogs; lignin was the best precursor, and cellulose the poorest. Carbohydrates were generally observed to be poor phenol precursors. The optimum temperature of phenol formation from wood lignin was shown to be in the region 500-600°C. Yields of phenol were higher in an atmosphere of nitrogen than in air.

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